

# Spin Dynamics in the Magnetic Chain Arrays of $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ : a Neutron Inelastic Scattering Investigation

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Below  $T \approx 150$  K, the spin arrangement in the chain arrays of  $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$  is shown to develop in two dimensions (2D). Both the correlations and the dispersion of the observed elementary excitations agree well with a model of interacting antiferromagnetic dimers. Along the chains, the intra- and inter-dimer distances are equal to 2 and  $\approx 3$  times the distance ( $c$ ) between neighboring Cu ions. While the intra-dimer coupling is  $J \approx 10$  meV, the inter-dimer couplings along and between the chains are of comparable strength,  $J_{\parallel} \approx -1.1$  meV and  $J_{\perp} \approx 1.7$  meV, respectively. This remarkable 2D arrangement satisfies the formal Cu valence of the undoped compound. Our data suggest also that it is associated with a relative sliding of one chain with respect to the next one, which, as  $T$  decreases, develops in the chain direction. A qualitative analysis shows that nearest inter-dimer spin correlations are ferromagnetic, which, in such a 2D structure, could well result from frustration effects.

An increasing interest is presently devoted to the compound  $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$  as superconductivity can be obtained in Ca doped materials under pressure [1]. This compound is also a remarkable spin system, which is made of two distinct magnetic structures [2]. One structure consists of an array of quantum ( $s = 1/2$ ) two-leg  $\text{Cu}_2\text{O}_3$  ladders and the other of an array of  $\text{CuO}_2$  quantum spin chains. These two mixed spin subsystems are expected to play a crucial role in the occurrence of superconductivity. An important and first question concerns the charge transfer process which takes place upon doping. Due to the formal Cu valence (+2.5), one expects holes to be already present in stoichiometric compounds. Recently, it has been proposed that, in such undoped materials, most of the holes are located in the chains [3]. This should result in a specific spin distribution in the chains. It is the purpose of the present neutron inelastic scattering (NIS) investigation to explore the actual spin arrangement in the chain arrays of the undoped compound. A good knowledge of the initial hole distribution is definitely required before any investigation of the hole-doping process be further developed. A few neutron investigations on undoped  $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$  have been previously performed. The first measurements were carried out on a powder sample [4]. The presence of magnetic excitations in the vicinity of 11 meV was confirmed, in agreement with susceptibility measurements [5]. They were attributed to the formation of antiferromagnetic (AF) dimers in the chains. The first measurements on a single crystal have revealed the presence of several excitation branches in the same energy range [6]. Their dispersion, which was determined in a limited part of

the Brillouin zone, provides evidence of interactions between the AF dimers in the chain direction. It was then proposed that the dimers are formed between spins separated by “2 and 4” times the distance ( $c$ ) between the nearest-neighbor Cu ions in the chains. In these measurements, however, the chosen scattering plane prevented any direct exploration of the chain arrays (fig. 1a). More recently, using a set of eight single crystals, new measurements were performed [8]. The dispersion along the chains was determined with an improved accuracy. The data were shown to compare well to a one-dimensional (1D) model of interacting AF dimers (also discussed in [10]), where the intra and inter-dimer distances ( $d$  and  $d'$ ), respectively) correspond to 2 or 3 times the distance  $c$ . Due to averaging effects inherent to the experimental procedure, again no information relative to any transverse directions could be obtained. In the present investigation, a unique single crystal was used and the measurements were performed on triple-axis spectrometers (IN8 and 1T1 at the Institut Laue Langevin in Grenoble and at the Laboratoire Léon Brillouin in Saclay, respectively). The orientation of the crystal was chosen in such a way that a rather exhaustive investigation of the chain arrays could be developed.

Our  $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$  sample was cut from a crystal several cm long grown by the travelling solvent zone method under a pressure of 3 bar oxygen atmosphere [11]. Its volume was about  $5 \times 5 \times 30$  mm<sup>3</sup> with the  $c$  axis in the longer dimension. The crystallographic structure of this material can be described with two distinct unitary subcells, one referring to the ladders, the other to the  $\text{CuO}_2$  magnetic chains. For the latter subcell - to be considered

hereafter - the space group and the lattice constants are at room temperature: *Amma*,  $a = 11.456$  Å,  $b = 13.361$  Å,  $c = 2.749$  Å, [2]. A sketch of the chain arrays in the (**a**,**c**) plane is shown in fig. 1a. In the **a** direction, one observes a doubling of the unit cell (the lattice parameter is twice the distance between chains) which is due to the relative shift (in the **c** direction) of one chain with respect to the next one [7,9]. This relative displacement is small at room temperature,  $\eta \approx 0.17c$  [7]. Most of our neutron measurements were performed with the scattering wavevector **Q** lying in the (**a**,**c**) plane. For inelastic scatterings, a horizontal collimation of 50'-50'-open-open was used, with a final wavevector  $\mathbf{k}_f = 2.662$  Å<sup>-1</sup>. Pyrolytic graphite single crystals were mounted as monochromator and analyser, and a pyrolytic graphite filter after the sample was used to eliminate higher-order flux contamination. Most of the energy scans reported here were performed in the range 2 – 20 meV with an energy resolution of the order of 1 meV (full width half maximum). The temperature could be varied from 1.5 to 300 K. In general, as shown in fig. 2a, two (and only two [6]) well-defined magnetic excitations are observed in the (**a**,**c**) plane at low temperature. For a few wavevectors, however, only a single excitation is detected. It is the case for the wavevectors  $\mathbf{Q} = (2.5, 0, Q_L)$ , where the unique line results from the superposition of two excitations (cf. fig. 2a which shows the single peak at  $Q_L = 0.25$ ). More surprisingly, it is also the case for the specific wavevectors  $(Q_H, 0, 0.65)$  (see fig. 2b) where an “apparent” extinction of one of the two modes occurs. Figs. 3a and 3b display the dispersions of the modes observed along the **a** and **c** directions, respectively. The former figure reports the data obtained at  $Q_H = 2$  and  $Q_H = 3$ . For these two values of  $Q_H$ , the data superpose very well yielding an excellent definition of the periodicity of the propagation along **c**. The latter figure displays a new and important result. Dispersive modes are also observed in the **a** direction. This result establishes unambiguously that a magnetic coupling does exist between the chains. As there are 2 non-equivalent neighboring chains in the **a** direction (they form a two-Bravais lattice), one is led to analyse the two observed branches (E' and E" in fig. 3b) as resulting from an unique excitation, which should be twice degenerated without such interchain interactions. The degeneracy is lifted by the interchain couplings and two propagative dispersions are observed. One branch is to be considered as the “image” of the other, shifted by one reciprocal lattice unit (r.l.u.)  $2\pi/a$  (see discussion below). In contrast to what is proposed in [6], the two branches do not result from the presence of possible magnetic anisotropies. On the contrary, the spin system describing the chains is to be considered as isotropic and, accordingly, the two branches are expected to be associated with a  $S = 1$  magnetic state. Under the effect of a magnetic field, they undergo an identical Zeeman splitting giving rise to a unique electron spin resonance

(ESR) line as observed experimentally [5]. With such an analysis, no contradiction is found between neutron and ESR data. Another striking result revealed by our measurements concerns the integrated intensity  $I_Q$  of the observed excitations. The values of  $I_Q$  measured in the chain direction are reported in fig. 4. Several features are worth being noted. In particular, extinction is seen to occur at specific values of  $Q_L$ : 0, 1/2 and 1. For instance, for  $Q_H = 3$  (fig. 4a), a double peak structure is seen in the first half of the Brillouin zone and a single peak structure in the second half. All these features must be taken into account in any analysis of the magnetic properties of the chains.

As a starting point of our analysis, we consider the 1D model of interacting AF dimers previously proposed [5,10]. In such a case, we may refer to the description of interacting excitons given in [12]. When the intra-dimer coupling  $J$  is much larger than the inter-dimer one  $J_{\parallel}$ , the energy dispersion along the chain is given by  $E/J \approx (1 - \alpha_{\parallel}^2/4) - \alpha_{\parallel}(1 + \alpha_{\parallel})\cos(m2\pi Q_L) + (\alpha_{\parallel}^2/4)\cos(m4\pi Q_L) \approx 1 - \alpha_{\parallel}\cos(m2\pi Q_L)$  with  $\alpha_{\parallel} = J_{\parallel}/2J$ . In that expression,  $Q_H$  is expressed in the r.l.u.  $2\pi/c$ , the inter-dimer distance is fixed to  $d = 2c$  (see discussion below) and the parameter  $m = [(d+d')/2]$  allows a determination of the inter-dimer distance  $d'$  relatively to  $d$ . A fitting procedure where  $J$ ,  $\alpha_{\parallel}$  and  $m$  are adjustable parameters is applied successively to the two sets of data in fig. 3. Within the experimental accuracy, identical values are obtained for  $\alpha_{\parallel}$  and  $m$ :  $\alpha_{\parallel} = -0.065 \pm 0.007$  and  $m = 4.95 \pm 0.3$ . Since  $\alpha_{\parallel} < 0$ , the inter-dimer coupling  $J_{\parallel}$  is deduced to be ferromagnetic (F) in that description. The value obtained for  $m$  suggests the inter-dimer distance  $d'$  to be practically equal to  $d' = 3c$  [8,10]. In that 1D description, different values are obtained for  $J$ :  $J_1 \approx 12.0$  meV and  $J_2 \approx 10.3$  meV for the upper and lower branches, respectively. As discussed above, however, the energy difference between the two branches results from the small dispersion observed in the transverse direction. Extrapolating the 1D description used above to the presence of small interchain couplings ( $J_{\perp} \ll J$ ), we can write the dispersion observed in the **a** direction as  $E/J \approx 1 - \alpha_{\perp}\cos(\pi Q_H + \varphi)$  with  $\alpha_{\perp} = J/2$  and where the phase factor  $\varphi$  ( $= 0$  or  $\pi$ ) accounts for the two transverse dispersive branches E' and E". Finally, after fitting the data in fig. 3b (the full and dashed lines with  $|\alpha_{\perp}| = 0.075 \pm 0.007$ ), one obtains the following set of values:  $J \approx 10$  meV,  $J_{\parallel} \approx -1.1$  meV and  $J_{\perp} \approx 1.7$  meV. It is established here that the couplings between AF dimers along **c** and along **a** are of comparable strength.

In a second step of our analysis, we consider the data of the integrated intensity  $I_Q$  reported in fig. 4. At low temperature, as higher energy excitations can be reasonably ignored, the quantity  $I_Q$  provides a good evaluation of the “structure factor”  $S_Q = \sum_n \langle s_n s_{n'} \rangle \exp[iQ(n - n')]$  where

$\langle s_n s_{n'} \rangle$  defines the static 2-spin correlation functions for spins located at sites  $n$  and  $n'$ . Since  $J_{\parallel}, J_{\perp} \ll J$ , one expects  $S_Q$  to be dominated by the intra-dimer correlations. Assuming the spins of a dimer to be located in a chain at sites  $n-1$  and  $n+1$ , the different intra-dimer correlations are about the same in absolute values, i.e.  $\langle s_{n\pm 1} s_{n\pm 1} \rangle \approx |\langle s_{n\pm 1} s_{n\mp 1} \rangle|$ . As the excitation energy ( $\approx 11$  meV) is large compared to the dispersion amplitude ( $\approx 1$  meV), the correlation length  $\xi$  of that quantum system is short ( $\xi \ll c, a$ ). Accordingly, as a first approach, we may limit the sum  $\Sigma_n$  to the inter-dimer correlations between nearest neighbors. Then, assuming (in the chain direction)  $\langle s_{n\mp 1} s_{n\pm 4} \rangle \approx \langle s_{n\pm 1} s_{n\pm 6} \rangle \approx -\langle s_{n\mp 1} s_{n\pm 6} \rangle \approx -\langle s_{n\pm 1} s_{n\pm 4} \rangle$ , we obtain from the correlations along the chains the expression  $I_Q \approx [1 - \cos(4\pi Q_L)][1 + 2\varepsilon_{\parallel} \cos(m2\pi Q_L)]$  where the first factor accounts for the intra-dimer correlations and  $\varepsilon_{\parallel}$  is the ratio between the inter- and intra-dimer correlations ( $\varepsilon_{\parallel} = \langle s_{n-1} s_{n+4} \rangle / \langle s_{n-1} s_{n-1} \rangle$ ). The first factor predicts zero intensities at  $Q_L = 0, 1/2, 1$ , exactly as it is experimentally observed (see fig. 4). This explains the value we have chosen above:  $d = 2c$ . In the second factor, the coefficient  $\varepsilon_{\parallel}$  is positive (negative) for AF (F) inter-dimer correlations. From the analysis of the dispersion curve presented above,  $\varepsilon_{\parallel}$  is expected to be negative and  $m \approx 4.5$ . For  $\varepsilon_{\parallel} = -0.2$ , one obtains the dashed line in fig. 4a. Interestingly, the double peak structure observed experimentally is reproduced qualitatively. In the whole Brillouin zone, however, the curve remains (almost) symmetric with respect to  $Q_L = 1/2$ . The occurrence of the double peak structure depends directly on the values of  $\varepsilon_{\parallel}$ : we evaluate  $0.15 \lesssim |\varepsilon_{\parallel}| \lesssim 0.25$ . Within the same simplified description, the effect of spin correlations between dimers located in neighboring chains can be described in a similar way and one is led to complete the above expression as (for simplicity, the magnetic form factor of the  $\text{Cu}^{2+}$  ions is ignored)

$$I_Q \approx [1 - \cos(4\pi Q_L)][1 + 2\varepsilon_{\parallel} \cos(m2\pi Q_L)][1 + 2\varepsilon_{\perp} \cos(\pi Q_H + m'\pi Q_L)]$$

where the last factor takes into account the relative displacement between neighboring chains:  $\eta = m'c/2$ . Similar to the previous case,  $\varepsilon_{\perp}$  is the ratio between transverse inter- and intra-dimer correlations. Depending on whether  $Q_H$  is even or odd, a phase factor is seen to be present or not in the cosine function in the last factor of  $I_Q$ . Considering first the  $I_Q$  data relative to the excitation branch E' observed at  $Q_H = 3$  (open dots in fig. 3a), a fitting procedure, with  $\varepsilon_{\perp}$  and  $m'$  as adjustable parameters ( $\varepsilon_{\parallel} = 0.2$  fixed), yields the continuous curve drawn in fig. 4a, and provides the following evaluations:  $\varepsilon_{\perp} = +0.36 \pm 0.06$  and  $m' = 1 \pm 0.1$ . The non symmetric behavior observed experimentally is now better reproduced in the whole Brillouin zone. The positive value obtained for  $\varepsilon_{\perp}$  (comparable to  $\varepsilon_{\parallel}$ , as expected) predicts the interchain correlations to be AF. Remarkable also is the value obtained for  $m'$  which shows that the relative

displacement  $\eta$  between neighboring chains is of the order of  $c/2$  at low temperature. In order to test further these predictions, the same model with all the above parameters fixed ( $\varepsilon_{\parallel} = 0.2$ ,  $\varepsilon_{\perp} = +0.36$  and  $m' = 1$ ) is applied to the  $I_Q$  data relative to the other excitation branches (figs. 4b and 4c). According to the description proposed above, the branch E'' observed at  $Q_H = 3$  (black dots in fig. 3) can be viewed as the "image" of the excitation branch E' at  $Q_H = 2$ . The corresponding structure factor is therefore to be described by the same expression as before but without the factor  $\pi$  in the last factor of  $I_Q$ . One obtains the full curve shown in fig. 4b (there is no additional adjustment except for an amplitude factor). Again the agreement appears to be reasonable in the whole Brillouin zone (for comparison, the curve obtained with the factor  $\pi$  is shown as the dashed line). Considering finally the data obtained at  $Q_H = 2$ , the structure factor relative to the branches E' and E'' (in fig. 3, the open and full squares, respectively) are also reasonably well explained by the same description: the full and dashed curves shown in fig. 4c are obtained with the factor  $\pi$  included and not included, respectively. The only noticeable discrepancy occurs for the low-energy data (full squares) in fig. 4c near  $Q_L = 0.65$ . Remember (cf. fig. 2b), it is also the  $Q_L$  region where an unexplained "apparent" extinction of one of the two branches occurs.

The relative displacement  $\eta$  can be supposed to vary with temperature. Such a change in the lattice structure could result in a simultaneous change in the spin arrangement. This seems to be the case as shown by the data reported in figs. 5a and 5b. The former figure represents the intensity  $A_Q$  of two nuclear Bragg peaks, observed at  $\mathbf{Q} = (4, 0, 0.3)$  and  $\mathbf{Q} = (3, 0, 0.3)$ . For the chains, these peaks correspond to the same  $Q_L = 0.3$ , but to different  $Q_H$  ( $= 3$  and  $4$ , respectively). Due to the doubling of the unit cell in the  $\mathbf{a}$  direction, Bragg peaks for even values of  $Q_L$  are expected not to be strongly affected by a variation of  $\eta$ . For odd values of  $Q_H$ , however,  $A_Q$  should decrease with  $\eta$  (it is equal to zero for  $\eta = 0$ ). Figure 5a agrees well with that description and confirms the picture suggested above, that neighboring chains are slowly sliding along  $\mathbf{c}$  as  $T$  decreases. Simultaneously, changes in the excitation spectrum are observed (see fig. 5b). In that figure, the energy of the single excitation shown in fig. 2b, is measured at  $Q_H = 3$  and  $Q_H = 2$ . Due to the transverse dispersion, two different values are obtained at low temperature. As  $T$  increases, however, they are seen to merge into the same value  $\approx 11.3$  meV, showing that the interchain coupling becomes ineffective above  $T \approx 150$  K.

The purpose of the analysis sketched above is to draw attention on the very peculiar spin distribution appearing in the chains of  $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ . At low temperature ( $T < 10$  K), the interactions between the AF dimers develop in two dimensions (2D). For the parameters de-

terminated above ( $d = 2c$ ,  $d' \approx 3c$  and  $\eta \approx c/2$ ), different spin arrangements can be proposed. However, as shown in fig. 1b, there exists one distribution which corresponds to a complete alternation in the spin dimerisation. It is remarkable that a similar situation is found in the dimerised phase of the spin-Peierls compound  $\text{CuGeO}_3$ , where a splitting in two excitation branches has also been recently observed [13]. For such a symmetric situation, however, if one of the inter-dimer couplings (or both of them) are assumed to be ferromagnetic, one is inevitably led to a misfit in the spin correlations, i.e. in the spin arrangement, as illustrated in fig. 1b. This picture suggests that frustration effects (typically AF couplings between next neighbor spins) might also play a role, offering then the possibility of alternative descriptions. Anyhow, to complete the above analysis, more theoretical and/or numerical studies are definitely required. The effect of Ca doping is expected to modify the charge distribution and therefore the spin arrangement in the chain arrays. For low doping levels (or non-stoichiometric oxygen contents for instance [14]) the presence of dimers can still be expected, but possibly with a smaller average inter-dimer distance  $d'$ . This could explain the periodicity of 2 and 4 reported in [6]. For stronger doping levels, however, more drastic changes should occur.

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FIG. 1. a) Schematic representation of a chain array in  $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ , with lattice parameters  $a$  and  $c$ .  $\eta$  is the relative displacement between neighboring chains; b) spin-dimerisation in the alternation model with an illustration of the spin correlations (see text). The full and open symbols represent Cu and O atoms, respectively

FIG. 2. Examples of chain excitation modes at low temperature ( $T < 4$  K): a) energy scans at  $(Q_H, 0, 0.25)$  and b) at  $(Q_H, 0, 0.65)$ .

FIG. 3. a) dispersion in the chain direction  $\mathbf{c}$  for excitations observed at  $Q_H = 2$  and  $Q_H = 3$  at low temperature ( $T < 4$  K); b) dispersion of the two excitations branches E' and E'' observed in the transverse direction  $\mathbf{a}$  ( $T < 4$  K). The lines are fitted curves (see text).

FIG. 4. Structure factors of the chain excitations as a function of  $Q_L$ : a) for the branch E' probed at  $Q_H = 3$ ; b) for the branch E'' probed at  $Q_H = 3$ ; for the branches E' and E'' (open and full symbols, respectively) probed at  $Q_H = 2$ . The lines are explained in the text.

FIG. 5. a) Intensity of the two nuclear Bragg peaks observed at  $(4, 0, 0.3)$  and  $(3, 0, 0.3)$  as a function of temperature; b) energy of the two excitation modes observed at  $(3, 0, 0.65)$  and  $(2, 0, 0.65)$  as a function of temperature. The lines are guides to the eye.

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